374. *Cation-exchange Resins. The Applicability of the Mass-action Law to the Exchange of Univalent Ions.*

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Methods are outlined for the determination of full exchange isotherms for univalent ions on ion-exchange resins.

The exchange of potassium, hydrogen, and ammonium ions on a sulphonated phenol–formaldehyde and a sulphonated cross-linked polystyrene resin has been studied. The nature of the resin and, in the case of the phenol–formaldehyde resin, its particle size have an effect on the affinity of the exchange process.

The applicability of the law of mass action to ion exchange is discussed and the findings of this investigation related to current theories of the mechanism of ion exchange.

ATTEMPTS have been made to predict and explain the behaviour of cation-exchange materials by using the Freundlich or Langmuir isotherms (Ungerer, *Kolloid. Z.*, 1925, **36**, 228; Boyd, Schubert, and Adamson, *J. Amer. Chem. Soc.*, 1947, **69**, 2818) or by assuming the operation of a Donnan equilibrium (Bauman and Eichhorn, *J. Amer. Chem. Soc.*, 1947, **69**, 2830). The phenomena of cation exchange can also be interpreted on a mass-action basis, and the mass-action law has been applied, with apparent success, to the more recent types of organic exchanger materials (Boyd, Schubert, and Adamson, *J. Amer. Chem. Soc.*, 1947, **69**, 2818; Kressman and Kitchener, *J.*, 1949, 1190).

The mass-action treatment has advantages over others in simplicity and clarity and it enables a thermodynamic constant to be evaluated which should be characteristic of any exchange on a given exchanger. For example, for the exchange of univalent cations on the hydrogen form of a cation-exchange resin :

$$\mathrm{H_R} + \mathrm{M^+{}_S} \rightleftharpoons \mathrm{M_R} + \mathrm{H^+{}_S}$$

(subscript R denoting resin phase, S solution phase) we may write :

$$Ka = \frac{X_R}{1 - X_R} \cdot \frac{1 - X_S}{X_S} \cdot \frac{f_{\mathrm{H^+}_S}}{f_{\mathrm{M^+}_S}} \cdot \frac{f_{\mathrm{M_R}}}{f_{\mathrm{H_R}}}$$

(where X_S = molar fraction of the cation M^+ in solution; X_R = molar fraction of the cation M^+ on the resin; and $f_{\mathrm{H^+}_S}$ and $f_{\mathrm{M_R}}$, etc., are the appropriate activity coefficients of the ions in solution and on the resin).

(To calculate X_S and X_R, the total molarity of the solution with respect to M^+ and H^+ must be known and similarly the total molar capacity, C_R, of the resin for these ions.)

No satisfactory method for evaluating activities in the resin phase has yet been published and all that can be derived at present from experimental data is :

$$K' = \frac{X_R}{1 - X_R} \cdot \frac{1 - X_S}{X_S} \cdot \frac{f_{\mathrm{H^+}_S}}{f_{\mathrm{M^+}_S}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the more common univalent ions in chloride solutions of total ionic strength less than 0·05 the ratio $f_{\mathrm{H^+}_S}/f_{\mathrm{M^+}_S}$ is only a few per cent. greater than unity and can generally be neglected without introducing serious error.

If an exchange isotherm for a resin is determined (the plot of X_R against X_S at a constant temperature) the value for K' can be calculated at any stage in the exchange process.

Kitchener and Kressman's work on the exchange of various cations with a sulphonated phenol–formaldehyde resin in its ammonium form indicated that the values of K' were practically constant, but the range of X_R values for which their constants were calculated was only about 0·4 to 0·7. Similarly, from the work of Boyd, Schubert, and Adamson the mass-action law would appear to be obeyed in the case of the sodium–hydrogen exchange over the range $X_R = 0{\cdot}3$ to $X_R = 0{\cdot}9$. However, in preliminary experiments in these laboratories on the exchange between hydrogen ions and the ions of lithium, sodium, potassium, ammonium, silver, and thallium on a sulphonated phenol–formaldehyde resin, it was found that values for K' varied considerably. In every case the value decreased by some 10—20% as X_R increased from 0·2 to 0·8.

A recent investigation by Duncan and Lister (*J.*, 1949, 3285; see also Faraday Society symposium on Chromatographic Analysis, 1949) on the exchange of sodium and hydrogen ions on Dowex 50 has confirmed the variability of the mass-action law constant with X_R, and Gregor (*J. Amer. Chem. Soc.*, 1948, **70**, 1293) predicts such a variability as a necessary outcome of most exchange processes.

The work described in this report was carried out with the object of determining the extent of the variability of K', as it is of considerable practical importance to know precisely what significance can be attributed to a mass-action law constant. This investigation has been restricted to an examination of the exchange of potassium, hydrogen, and ammonium ions (especially the first two) on two types of resin, a sulphonated cross-linked polystyrene and a sulphonated phenol–formaldehyde resin. The results reported here largely confirm the findings of Duncan and Lister and in addition may throw some light on apparent anomalies in the results of various workers in this field.

GENERAL TECHNIQUE.

A. *Progressive-batch Method.*—A sample of 2—5 g. of dry hydrogen-form resin, of exchange capacity C_R milliequivalents (an amount possessing an exchange capacity of about 10 milliequivalents should be used), is placed in a dry 250-ml. conical flask, and Y ml. of a solution of the exchanging ion M^+, diluted to 125 ml. with water, are added. The solution of M^+ used contains m milliequivalents of ion per ml. The resin and solution are then shaken mechanically in a thermostatically controlled water-bath until no further exchange takes place.

A fraction, f, of the resulting solution is removed and the number of milliequivalents of hydrogen ion, x_1, in this aliquot determined by titration with standard alkali (approximately 0·05N.). If the resin is in the form of fine particles the aliquot, f, should be pipetted through a small sinter kept permanently in the flask.

To the remaining solution in contact with the resin b . Y ml. of standard M^+ solution are added and the volume again adjusted to 125 ml. with water. After equilibrium has been reached for the second time at the correct temperature a further aliquot f is removed and the number of milliequivalents of hydrogen ion now present, x_2, determined.

Similarly for the nth experiment, b^{n-1} . Y ml. of M^+ solution are added and the number of milliequivalents of H^+, x_n, in the nth aliquot is determined by titration. With such an experiment it can be proved that after the nth exchange

$$X_{B_n} = \left(f \,.\, \sum_{i=1}^{i=n-1} (x_i) + x_n\right)\Big/ f \,.\, C_B \quad . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (2)$$

and
$$X_{S_n} = 1 - \{x_n\,(1 - f - b)/f.m.Y[(1 - f)^n - b^n]\}$$

The expression for X_{S_n} can be simplified by grouping the constants to form a factor t_n, where $t_n = (1 - f - b)/f[(1 - f)^n - b^n]$, which can be calculated for each value of n when the values for f and b are decided upon, and hence:

$$X_{S_n} = 1 - t_n \,.\, x_n/m \,.\, Y \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (3)$$

Thus by use of equations 2 and 3 an isotherm can easily be constructed from a series of simple titration experiments. For most univalent exchanges it is found that a value of 1·25 for b gives a suitable spacing of points on an isotherm. In order to keep the total ionic strength of solutions to a minimum, so as to avoid the necessity of making activity corrections, f should be at least 0·8 (a 100 ml. portion from 125 ml. has been used in this work). The best value for Y depends upon the value for K' and it can be shown that for the first point on the isotherm to be at $X_B = 0{\cdot}125$, Y should be equal to $(C_B/56K' \,.\, m)(1 + 7K')$. Clearly b^{n-1} . Y must not exceed 100 ml., *i.e.* Y should not be greater than about 15 ml. for an 8-point isotherm.

A technique similar to that outlined above can be used when the resin is in the M^+-saturated form, b^{n-1} . Y ml. of acid solution containing m milliequivalents of H^+ per ml. being added, and the number of the milliequivalents of hydrogen ions in the aliquot f again being determined. These experiments check the "forward" isotherm (first point $X_B = 0{\cdot}125$) by a "back" isotherm (first point $X_B = 0{\cdot}875$). The formulæ for calculating X_{B_n} and X_{S_n} are similar to 2 and 3 above, viz:

$$X_{B_n} = \left(\sum_{i=1}^{i=n} (m \,.\, Y)b^{i-1} - \sum_{i=1}^{i=n-1} (x_i) - x_n/f\right)\Big/ C_B \quad . \; . \; . \; . \; . \qquad (4)$$

$$X_{S_n} = 1 - t_n \,.\, x_n/m \,.\, Y \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (5)$$

with the m and Y values referring to the acid added.

The value for C_B used in equations (2) and (4) is best determined from the titrations actually made during the determination of the isotherm. For example, if after the determinations of the last point on a "forward" isotherm of the exchange of M^+ with H_B, the resin is transferred quantitatively to a tube and the remaining hydrogen ion eluted by a strong solution of M^+, then:

$$C_B = \sum_{i=1}^{i=n-1} (x_i) + \frac{x_n}{f} + E$$

where E is the number of milliequivalents of hydrogen ions removed from the resin.

Clearly, although most convenient for exchanges involving the hydrogen ion, the technique outlined above can be used for any other univalent exchange, the titration with standard alkali being replaced by a suitable determination of the ion used in place of the hydrogen ion.

It has been found that, owing to experimental errors, accurate values of K' cannot be calculated from the first point in either the "forward" or "backward" determination and, for the same reason, no value for X_S outside the range 0·125—0·90 should be used. All points on the isotherm of X_B value greater than 0·9 or less than 0·2 should be rejected.

B. *Single-batch Method.*—To check any one point on an isotherm, the X_B and the X_S value can be determined in a single experiment by equilibrating a resin of known capacity, C_B milliequivalents, with a solution of known initial X_S value and determining the amount of one of the ions remaining in the solution. Thus if a solution which initially contains A milliequivalents of M^+ and B_1 milliequivalents of H^+ is equilibrated with a resin in the hydrogen form and is thereafter found to contain B_2 milliequivalents of H^+

$$X_S = (A + B_1 - B_2)/(A + B_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$X_R = (B_2 - B_1)/C_R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If the amount of M^+ in the solution in equilibrium with the resin is also directly determined and not assumed to be equal to $A - (B_2 - B_1)$, then a complete check can be made on the quantitative nature of the exchange and any adsorption phenomena revealed. As deposition on apparatus walls, etc., can be assumed to be absent with univalent ions, it is not necessary to analyse directly the resin phase. Such analysis would probably only introduce unnecessary error.

Although useful for single-value determinations and for the confirmation of quantitative ion exchange, the above technique is less suitable than the progressive-batch method when it is desired to determine a complete isotherm. The progressive batch method is considerably more rapid and convenient, and is more economic in the use of both resin and exchanging ions.

C. *Column Method.*—The progressive-batch method is not sufficiently accurate for a satisfactory determination of points at either extreme of an isotherm, *i.e.*, where X_R is less than 0·2 or greater than 0·9, and the single-batch method necessitates the use of undesirably concentrated solutions and is somewhat inconvenient when several determinations have to be made. For the determination of X_R and X_S at either end of the isotherm a procedure has been devised in which a solution of known X_S value is used and the X_R value of the resin in equilibrium with this solution is determined.

In this method, which will be called the column method, about 10 milliequivalents of resin are placed in a glass tube so as to make a column 5—10 cm. long. The column is jacketed with water at a thermostatically controlled temperature and a solution of known X_S composition and correct temperature is poured through the tube at a rate of 5—6 ml. a minute until the resin has assumed the correct equilibrium composition. The resin used is initially saturated by the ion of which it will finally contain most. Finally the resin is slowly washed with water until the eluent is ion-free.

To ensure reasonably rapid attainment of equilibrium at least 0·2M-solutions must be used. These are too strong for activity corrections to be neglected but the resin while being washed will to some extent equilibrate with progressively more dilute solutions until its composition is probably not far removed from the " ideal " value.

Points on an isotherm can now be plotted, as the values for X_S are already known and the X_R values can be obtained by suitable analysis of the resin column. For example, if the column has been used to obtain an X_R value for the H_R to M_R change with X_R small, the M on the resin is eluted by strong acid and the eluent analysed for this ion. The total capacity of the resin in the column is then determined by eluting it with a strong solution of M^+ ions and determining the amount of acid in the eluent. The resin is then in a condition in which it can be used to obtain a point at the other end of the isotherm.

EXPERIMENTAL.

Materials Used.—Potassium and ammonium ions were used as standard solutions prepared directly from the dried AnalaR quality chlorides. Hydrochloric acid solutions were prepared from AnalaR material and standardised against anhydrous sodium carbonate.

The resins used were Zeo-Karb 215, a sulphonated phenol–formaldehyde manufactured by Permutit Ltd., and a sulphonated cross-linked polystyrene of a similar type to Dowex 50. The latter, which was prepared at the Chemical Research Laboratories, Teddington, and supplied by courtesy of the Director, will be referred to as the C.R.L. resin. It was used, as received, in the form of spherules of uniform size (passing B.S. 100 sieve but retained by B.S. 150) the capacity being about 5 milliequivalents per g. of dry resin. The Zeo-Karb resin was carefully ground and two fractions used, one passing B.S. sieve 12 but retained in B.S. 25 and the other passing B.S. 60 but retained on B.S. 150. These fractions will be referred to as coarse and fine Zeo-Karb, respectively. The capacity of the Zeo-Karb resin was about 2 milliequivalents per g. of dry resin. Before use the resins were packed into columns and eluted alternately with 2N-sodium chloride solution and 2N-hydrochloric acid, the cycle being repeated at least twice. The resins were finally washed thoroughly with re-distilled water.

Conditions for Equilibrium.—In the single- and progressive-batch experiments it was found that no appreciable increase in the amount of exchange took place after shaking the resins for 1½ hours in contact with a solution of potassium chloride.

This was shown to apply to both the coarse Zeo-Karb and the C.R.L. resin at 20°, and to apply irrespective of whether the resin was in the hydrogen or potassium form. All batch experiments were therefore assumed complete after 100 minutes' shaking.

In the column experiments the composition of the resin was the same whether 1000 ml. or 500 ml. of solution had passed, and the latter volume was therefore assumed to be sufficient.

FIG. 1.

K^+/H^+ *exchange on fine Zeo-Karb* 215 *at* 20°.

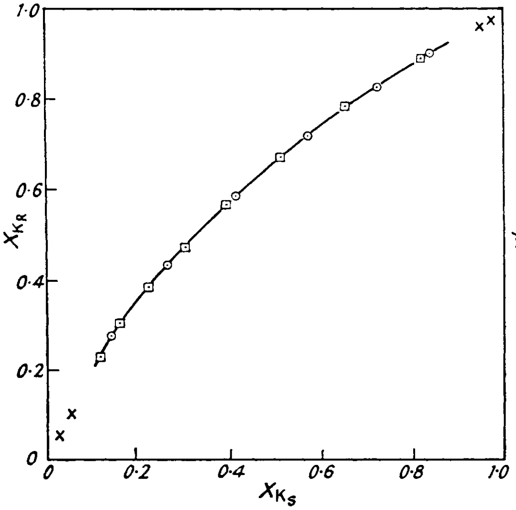


FIG. 2.

K^+/H^+ *exchange on coarse Zeo-Karb* 215 *at* 20° *and* 30°.

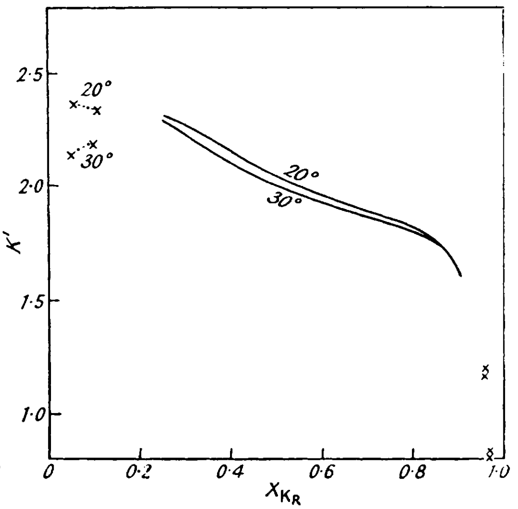


FIG. 1. ○ *Forward progressive batch.* ⊡ *Backward progressive batch.* × *Column.*

FIG. 3.

K^+/H^+ *exchange on fine Zeo-Karb* 215 *at* 20° *and* 30°.

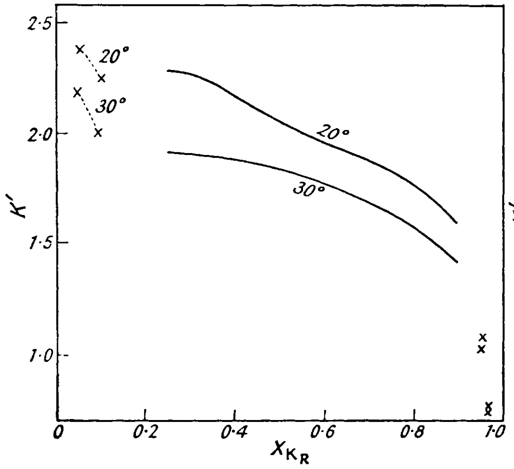
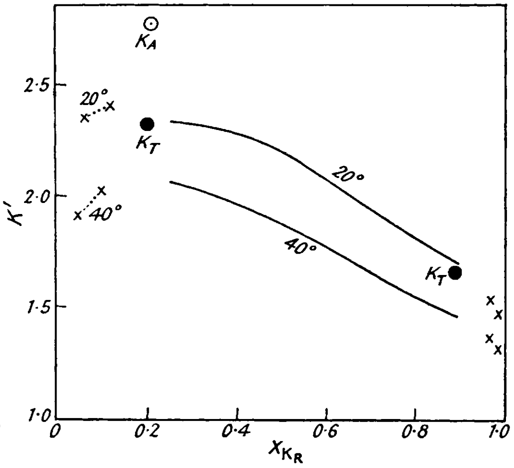


FIG. 4.

K^+/H^+ *exchange on C.R.L. resin at* 20° *and* 40°.



A slight hydrolytic decomposition of the Zeo-Karb resin when in the hydrogen form was initially rather confusing and mistaken for continued exchange. However, it was found that this hydrolysis could be corrected for in progressive-batch experiments by carrying out a blank. The amount of acid in this blank was proportional to the fraction of resin in the hydrogen form and hence suitable corrections could be made at any X_R value from a blank carried out on the resin entirely in the hydrogen form.

Methods of Analysis.—Hydrogen-ion concentrations were determined in all experiments by titration with standard alkali.

The ammonium-ion concentration was determined volumetrically by the addition of a known excess of standard alkali followed by determination of the amount left after removal of ammonia by boiling. When hydrochloric acid was also present any large excess of this acid was removed by careful evaporation, and the remainder neutralised before addition of the standard alkali.

Potassium, when present only with hydrochloric acid, was determined by removing all acid by repeated evaporation with water, and then estimating the chloride left by titration with mercuric nitrate.

A blank compensated for traces of non-volatile chlorides formed by the action of hydrochloric acid on glass, etc. When potassium was present with ammonium salts the latter were replaced by sodium by boiling the solution with sodium hydroxide solution and the potassium in the resulting mixture determined as the perchlorate. After the salts had been heated to fuming with a very slight excess of perchloric acid to convert the chlorides into perchlorates, these were extracted with dry ethyl acetate to remove the sodium salt. To compensate for traces of potassium and ammonium introduced during the analysis, each determination was standardised by the simultaneous analysis of a synthetic mixture of similar composition, containing a known amount of potassium.

FIG. 5.

NH_4^+/H^+ *exchange on C.R.L. resin at* 20°.

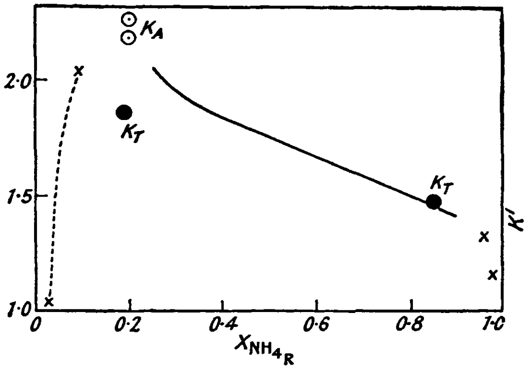
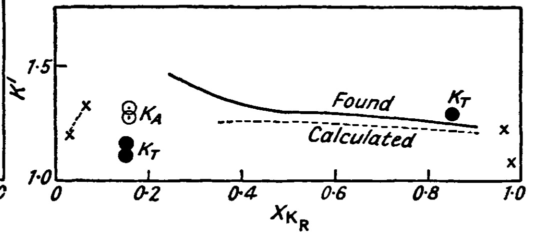


FIG. 6.

K^+/NH_4^+ *exchange on C.R.L. resin at* 20°.



Experimental Data.—The experimental data obtained in this investigation are summarised diagrammatically in Figs. 1—6. Fig. 1 shows a typical isotherm obtained by the progressive-batch method with points obtained by column experiments at each end. Mass-law constants for each exchange studied have been calculated at regular X_R intervals from the best curve through the plot of progesssive-batch experimental data. A plot of K' against X_R is shown by the continuous lines in Fig. 2—6. K' values from column experiments are shown in these diagrams by crosses.

In addition to the above experiments; single-batch experiments were made with all the exchanges possible between potassium, hydrogen, and ammonium ions, by using the C.R.L. resin at 20°. The results of full analyses of the aqueous phases, before and after exchange, are shown in Tables I—III. Two mass-action law constants have been calculated from these data. K_A is the value which would be calculated solely from a consideration of the quantities of exchanged ion,* as is done in the progressive-batch experiments. K_T is the " true " exchange constant calculated from a consideration of the actual ionic composition of both resin and solution. These two K values are also shown in Figs. 4—6. 250 Ml. of solution and 3 g. of resin were used in the experiments at low X_R; in the experiments at high X_R value 400 ml. of solution and 1·5 g. of resin were employed.

TABLE I.

Potassium hydrogen exchange, C.R.L. resin at 20°.

Composition of solution (milliequivalents of ion), initial solution.		final solution.		Exchange.		Mass-law constants.	
K^+.	H^+.	K^+.	H^+.	K^+ (on).	H^+ (off).	K_A.	K_T.
3·004	5·120	0·808	7·410	2·196	2·290	2·77 (X_R = 0·211)	2·32 (X_R = 0·202)
25·00	0·00	20·69	4·34	4·31	4·34	—	1·66 (X_R = 0·888)

TABLE II.

Ammonium/hydrogen exchange, C.R.L. resin at 20°.

NH_4^+.	H^+.	NH_4^+.	H^+.	NH_4^+ (on).	H^+ (off).	K_A.	K_T.
3·000	5·000	0·917	7·175	2·083	2·175	2·18 (X_R = 0·200)	1·86 (X_R = 0·192)
3·004	5·120	0·932	7·310	2·072	2·190	2·26 (X_R = 0·201)	1·85 (X_R = 0·191)
24·98	0·00	19·95	5·04	5·03	5·04	—	1·47 (X_R = 0·853)

TABLE III.

Potassium/ammonium exchange, C.R.L. resin at 20°.

K^+.	NH_4^+.	K^+.	NH_4^+.	K^+ (on).	NH_4^+ (off).	K_A.	K_T.
3·000	7·000	1·347	8·740	1·653	1·740	1·32 (X_R = 0·160)	1·17 (X_R = 0·153)
3·000	7·000	1·390	8·70	1·610	1·700	1·28 (X_R = 0·160)	1·12 (X_R = 0·152)
25·00	0·00	20·35	4·56	4·65	4·56	—	1·30 (X_R = 0·852)

* When an ion M_1^+ displaces an ion M_2^+ from a resin the reaction will be referred to for brevity as the M_1^+/M_2^+ exchange, M_1^+ being called the exchanging ion and M_2^+ the exchanged ion.

DISCUSSION.

It is clear from the figures that no mass-action law constant for the simple exchanges studied in this investigation can be calculated by using equation (1). Although, as suggested by Kitchener and Kressman (*loc. cit.*), changes of activity of an ion in solution may be compensated for by activity changes of the ion in the resin phase, the activity of the resin phase *per se* is itself not constant, even in dilute solutions, and varies with the ionic composition of the exchanger. This has already been considered by Kieland (*J. Soc. Chem. Ind.*, 1935, **54**, 232; *Tids. Kjemi*, 1935, **15**, 74) for inorganic exchangers. The correction suggested by him, which leads to the expression :

$$\log K' = \log Ka - C(1 - 2X_{\mathrm{R}})$$

where Ka is the true thermodynamic exchange constant and C an "activity correction" constant, applies fairly well over the range $X_{\mathrm{R}} = 0{\cdot}35$—$0{\cdot}75$ but fails badly outside it. At present it is doubtful whether any practical activity correction can be devised which will apply over the whole isotherm.

In part at least this is due to phenomena other than true exchange taking place, as will be seen from a consideration of the experimental data.

The K' values obtained from column experiments at a small X_{R} value were determined by measuring the amount of exchanging ion on the resin, and they thus measure true exchange together with any adsorption of the exchanging ion. In these circumstances adsorption equivalent to only a few per cent. of the exchange capacity of the resin is sufficient to cause a considerable increase in the apparent value of K'. A similar measurement is made in Duncan and Lister's "break-through volume" method and from the "hump" in the plot of K' against X_{R} obtained by these authors it would appear that, in the sodium/hydrogen exchange, true exchange is taking place together with a variable amount of adsorption, the latter being at a maximum at $X_{\mathrm{R}} = 0{\cdot}1$—$0{\cdot}2$. In our own investigation points to the left of such a maximum have in general been obtained, although for the exchange on coarse Zeo-Karb at 20° and fine Zeo-Karb at 20° and 30° the points appear to be situated on the peak or to the right thereof. Apart from adsorption phenomena it may well be that the true exchange constant is itself decreasing with X_{R}, as witness the exceptionally low value of K' at $X_{\mathrm{R}} = 0{\cdot}024$ in the NH_4^+/H^+ exchange (Fig. 5).

K' values from progressive-batch experiments, over the range $X_{\mathrm{R}} = 0{\cdot}4$—$0{\cdot}9$, approximate closely to true exchange constants. This is probably also the case with K' values obtained from column experiments at high X_{R}. The latter have been calculated from a determination of the quantity of exchanged ion still left on the resin and could therefore be spuriously low in the event of an adsorption of the exchange ion taking place.

The K_T values from single-batch experiments also confirm, within experimental error, the general trend of the isotherms, but it will be noted that the K' values are high and there appears to be more exchanged ion leaving the resin than exchanging ion going on to it. This effect is probably the result of water being absorbed by the resin and not, as might be supposed, from a desorption of exchanged ion. In those experiments shown in the tables which were made at a low X_{R} value 3 g. of air-dried resin were added to 250 ml. of solution. The amount of pure water absorbed from the electrolyte solution by this resin is difficult to estimate exactly but it is probably sufficient (1·5—2·5 ml.) to account for the apparent non-equivalence of exchange and to reduce K_A values to those of K_T, the latter being substantially unchanged.

Methods depending solely upon the measurement of the exchanged ion in an aliquot of solution are therefore very sensitive at low X_{R} to the absorption of water by the resin, unless a very high liquid-to-resin ratio is maintained or the amount of pure water effectively withdrawn into the resin phase is accurately known. With the column experiments this error is not incurred and by neglecting it in the progressive-batch experiments the general shape of the K' against X_{R} plot is not significantly changed except at low X_{R} values. The first plotted points are here probably sufficiently in error to account for the comparatively sudden rise in K' found in some experiments at values of X_{R} less than 0·3—0·4. Values from K' at $X_{\mathrm{R}} = 0{\cdot}5$ would be only 2—3 per cent. too large.

Apart from the above outline of exchange behaviour, some of which requires further experimental confirmation, there are certain other points of interest arising from this work.

The whole question of the mechanism of ion exchange has recently been dealt with by two different methods of approach. Kitchener and Kressman have suggested that a univalent-ion exchange may arise chiefly from the difference in coulombic energy of the two possible ion-resin electrostatic bonds. Presumably this energy difference is responsible for much of the maximum work of the exchange, any expansion or contraction of the resin matrix being ignored. On the other hand Gregor (*J. Amer. Chem. Soc.*, 1948, **70**, 1293) interprets exchange phenomena on the basis of osmosis, no direct interaction of exchanging and fixed " resin ions " being postulated. The resin is said to undergo a volume change ($V_{M^+_2} - V_{M^+_1}$) due to osmotic pressure, and by equating the virtual osmotic and PV work at equilibrium the expression :

$$RT \ln (a_{M^+_1}/a_{M^+_2})_R \cdot (a_{M^+_2}/a_{M^+_1})_S = p(V_{M^+_2} - V_{M^+_1})$$

is derived, where p is the swelling pressure.

It is of interest that both the above interpretations can be considered to be based upon the relationship :

$$\Delta G = \Delta A + \int p\mathrm{d}v.$$

where $\int p\mathrm{d}v$ is the work done against the external osmotic pressure, p, ΔG is the free energy and ΔA the work function. According to the first interpretation, ΔG is assumed to be equivalent to the maximum work done in replacing one ionic binding with another, assuming no significant volume changes; according to the second, the maximum work function term is neglected and the change in free energy assumed equal to the work of contraction or expansion of the resin against osmotic pressure. The two mechanisms are not necessarily mutually exclusive and it would be desirable to know to what extent they each contribute to exchange phenomena. The data for evaluating the difference in coulombic energy of ions as they exist on the resin are not known and it remains to be seen precisely how well affinity constants can be predicted from osmotic data.

The results of the present work are of some value in deciding which of the two mechanisms predominates during exchange from dilute aqueous solutions.

In the absence of activity correction data, true thermodynamic constants cannot be evaluated from K', but for comparison purposes between different resins etc., by using the same exchange reaction, it is probably legitimate to make use of the exchange constants at some fixed X_R value, say 0·5. Thus with the potassium/hydrogen exchange on the C.R.L. resin and on the coarse and fine Zeo-Karb 215 resin (Fig. 2, 3, and 4) it will be seen that data are available for calculation of the standard decrease of free energy of exchange, $-\Delta G^\circ$. If the simple form of the reaction isochore can be used over the temperature range 20—40° an approximate value for the heat of reaction ΔH° may also be computed and hence the change of " bound heat " $T\Delta S^\circ$ evaluated from the equation $-\Delta G = -\Delta H + T\Delta S$. The approximate values of $-\Delta G^\circ$, $-\Delta H^\circ$, and $-T\Delta S^\circ$ at 20° for X_R 0·5 are given in Table IV.

TABLE IV.

Resin.	$-\Delta G^\circ$ (kcals.).	$-\Delta H^\circ$ (kcals.).	$-T\Delta S^\circ$ (kcals.).
C.R.L.	0·46	1·45	1·0
Fine Zeo-Karb 215	0·42	2·0	1·6
Coarse Zeo-Karb 215	0·41	0·25	−0·15

It will be seen that the decrease of free energy at 20° is significantly greater with the polystyrene resin than with Zeo-Karb 215, and this has been found to be the case with all univalent-ion exchanges studied. One explanation of such behaviour is that there is an appreciable difference in the " distance of least separation " of the two exchanging ions (or the sulphonic groups on the resin) in the two materials. Alternatively, the difference could be explained by the increase in expansion possible with the more elastic polystyrene resin and it would be interesting to determine the variation of exchange constant with the degree of cross linkage of these polymers.

The most striking feature shown in Table IV, however, is the significant differences in the decrease of bound heat in the three reactions studied. This not only varies from the one resin to the other but, more important, is markedly different with the two samples of Zeo-Karb 215. These were from the same bottle of resin and differed only in particle volume (by a factor of about 50—100). As mentioned by Kitchener and Kressman, if entropy changes in the resin can be ignored this alteration of bound heat must arise from a change in the degree of hydration of the ions during the exchange. A change of only 1—2 kcals., however, seems rather small considering that the heat of hydration of these ions is of the order of 100—200 kcals. and even if the differences in hydration varied for the same exchange on two essentially different types of resin, it is difficult to understand how a relatively small particle-size variation in the same sample of resin could have any effect. On the other hand, if part at least of the entropy change were associated with resin expansion and contraction, the variation between the two types of resin and between the two samples of the same resin would be more easily understandable. In the latter case, although ideally the change of bound heat for a gram-equivalent exchange should not depend upon the subdivision of the exchanger, in practice the differences of internal strain and surface energy, etc., between bulks of resin comprised of large and small pieces might well give rise to such an effect.

There remains to be considered the marked variation of K' with X_R. This may arise from a progressive decrease in the effective radius of the hydrogen ion in comparison with that of the potassium ion, but, as mentioned above, one would expect significant changes of this nature to be accompanied by a considerable heat of reaction. Gregor explains the variation on the grounds that the virtual pV work is not a constant and varies with the degree of exchange. Certainly the very marked difference between the behaviour of the C.R.L. and the Zeo-Karb resins at high X_R might well arise from the difference in elastic properties of these materials.

Whichever mechanism predominates the potassium/ammonium exchange (between ions of similar radii whether hydrated or otherwise) would be expected to be nearly unity and to vary little with X_R. It is interesting to note that the variations of K' with X_R for the potassium/hydrogen and ammonium/hydrogen exchanges, over the portion of the isotherm unaffected by any water absorption, effectively compensate each other. Values for K' for the potassium/ammonium exchange calculated from the ratio of these constants, as if they were true thermodynamic constants at any X_R value, are in excellent agreement with the experimentally determined figures (see Fig. 6).

Thus, although they are not, strictly speaking, thermodynamic constants, the values for K' at an X_R value of about 0·5 are of practical use in comparing exchange behaviour between various pairs of ions and various exchangers. However, the use of constants determined in this region for the prediction of analytical separations by, for example, Mayer and Tompkins's method (*J. Amer. Chem. Soc.*, 1947, **69**, 2866) is impracticable. Affinity constants for use when working at either end of the isotherms must be determined under conditions approximating as nearly as possible to those to be used during the proposed separation.

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